Giant X-Ray Absorption Circular Dichroism in Magnetic Ultrathin Films of Fe/Cu(001)

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Extraordinarily large circular dichroism has been observed in the near-edge x-ray absorption of the Fe $2p^{3/2}$ and $2p^{1/2}$ lines of monolayer magnetic films of Fe on Cu(001). This is the first reported observation of normal incidence dichroism in a metal overlayer. Analysis of such large variations using a simple and concise theoretical formulation suggests a saturation of the dichroism effect. This analytical approach also permits an approximate determination of the magnetic moment directly from experimental parameters.

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One of the basic thrusts of the investigation of nanoscale magnetic structures is the establishment of structure-property relationships. Ordinarily, efforts to measure nanoscale magnetic properties in conjunction with atomistic geometric and electronic structures runs headlong into the same problem: The magnetic perturbation tends to be a small component of the overall effect. In contrast to this, here we report giant circular dichroism in the near-edge core-level x-ray absorption of a near-monolayer metal film. An example of our data is shown in Fig. 1. (Because the magnetization and x-ray incidence are normal to the surface, we call it perpendicular dichroism.) This is a direct measurement of the spin polarization and the density of the unoccupied states near E_F in a ferromagnetic system.

Although the size of this effect is quite remarkable, and the observation of perpendicular dichroism in monolayer ultrathin films is novel and significant, it is consistent with earlier experiments and recent observations. Previous studies [1] of soft-x-ray magnetic circular dichroism (MCD) with monolayer films (exhibiting parallel dichroism with the magnetization and x-ray direction parallel to the surface) typically displayed a few percent effect, and magnetic multilayers have also demonstrated a very large circular dichroism [2]. It is important that, in terms of peak height asymmetries, our perpendicular dichroism effect is 20% to 40%, while the in-plane or parallel dichroism (with the x rays at grazing incidence) of other monolayer films is typically 2% to 6% (Ref. [1]). Even the asymmetry of bulklike Ni samples, which have exhibited an 11% effect, are a factor of 2 to 4 smaller than the Fe/Cu(001) case. It will be shown that our work with Fe/Cu(001) is in accordance with studies of the same system using spin-polarized electron spectroscopies [3] and surface magneto-optic Kerr effect measurement [4]. Fe/Cu(001) is a system with considerable history and controversy [3–7], in particular, having to do with growth modes and coverage determinations [3–6]. While the coverage dependences of our MCD results match those of others [3,4], fine-tuned absolute coverage determinations are not of central importance to this study. In addition, it is important to note that the selectivity of circularly polarized x rays can actually substitute for spin selection in the detection process [8], and that while the Fe L edges displayed a large MCD effect, none was observed in the corresponding Cu L edges, which is a

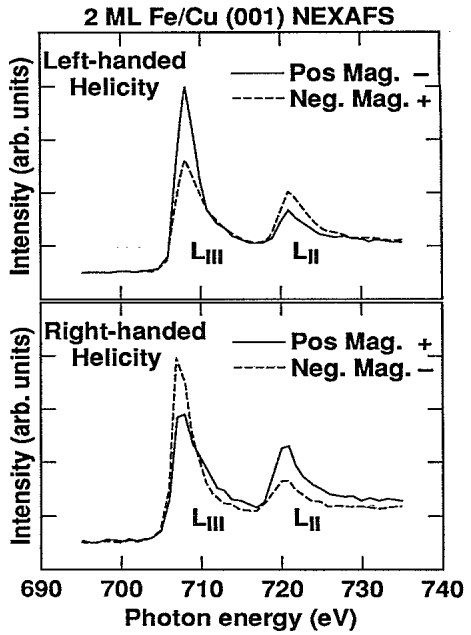

FIG. 1. The near-edge x-ray-absorption fine-structure (NEXAFS) dichroism of 2 ML of Fe/Cu(001). These are plots of absorption vs photon energy. The upper panel shows the effect of reversing the magnetization while maintaining the left-handed helicity of x rays. Similarly for the lower panel and right-handed helicity x rays. Samples are perpendicularly magnetized either into (positive magnetization) or out of (negative magnetization) the surface. The symbol + (−) means that the helicity and magnetization are parallel (antiparallel). The $2p^{3/2}$ peak is at the L_{III} edge and the $2p^{1/2}$ peak is at the L_{II} edge. The spectra were normalized to each other by equating the preedge intensity, at energies below approximately 700 eV.

demonstration of the elemental selectivity of x-ray absorption.

The experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) using the spherical grating monochromator of beam line 8-2, which is part of the facilities of the University of California/National Laboratories Participating Research Team (UC/NL-PRT). This is a bending magnet beam line, where the circular polarization of the x rays is obtained by moving the first mirror so that x rays above or below the horizontal plane are selectively accepted [1,9,10]. Wu *et al.* [2] demonstrated the feasibility of this operation with the BL8-2 SGM. The x rays were at normal incidence, which generally meant that the Poynting vector of the x-ray beam was parallel or antiparallel to the remnant magnetization of the Fe/Cu(001), which is typically perpendicular to the surface. (The normal incidence geometry probably aids in the retention of helicity as the x rays enter the sample, because of the absence of any component of the electric vector perpendicular to the surface.) The absorption process was monitored by counting electrons [11] in a window near kinetic energy (KE) of 47 eV, thus emphasizing the contribution from the *MVV* Fe Auger electrons. The results were reproduced several times. The NEXAFS measurements were normalized to photon flux via dividing by the output of an upstream I_0 detector, based upon a 95% transmitting grid of gold. Circular polarization detectors (CoPd multilayers, provided by IBM [2]), were mounted in the I_0 section to confirm the success of the mirror movement operation to do a helicity selection. The ultrathin films were magnetized perpendicular to the surface by following the recipes in Ref. [3], using a magnetic pulse on the order of 3 kOe. Sample preparation, including cleaning and Fe evaporation, is described elsewhere [11]. We conservatively project a factor of 2 uncertainty in all absolute coverage estimates [5,6,11], which does not strongly impact the results of the MCD study [11]. Base pressure was 2×10^{-10} torr.

Now, let us return to consider the data in Fig. 1 more quantitatively. Again, the key parameter is whether the magnetization and helicity are parallel or antiparallel, regardless of whether they are aligned into or out of the surface. Although the apparent edge jump shifts with mirror position, the front edge of the $2p^{3/2}$ peak is the same for a given helicity (and thus mirror position) regardless of magnetization. This demonstrates the advantage of keeping all else the same and flipping the magnetization of a given sample with a large pulsed field. The NEXAFS spectra taken with linear polarization (not shown) appear to be a sum of the two circular polarization extremes, as would be expected. Because of mirror motion and sample repositioning, the absolute intensity relationships between individual spectra has been compromised. Thus, the quantitative analysis will be couched in terms of branching ratios of the $2p^{3/2}$ to $2p^{1/2}$ intensities within a given spectrum ($B=I(2p^{3/2})/[I(2p^{3/2})+I(2p^{1/2})]$) (Ref. [12]). Branching ratios are derived from peak areas, using a linear background, two step functions, and two peak functions. Peak areas could be determined with an error of about 2%, thus experimental branching ratios have errors of 4% or less. A summary of this information is shown in Table I, under $B_{\rm exp}$.

Our approach in analyzing these results is to break the branching ratio problem into two parts: (1) the "nonstatistical" component and (2) the helicity dependence. It has been previously observed [12] that linear-polarization branching ratios are nonstatistical (i.e., not $\frac{2}{3}$ for $I(2p^{3/2})/[I(2p^{3/2})+I(2p^{1/2})]$), as would be expected

TABLE I. A comparison of experimental and theoretical branching ratios. The symbols are as follows: *P*, polarization; *L*, left; *R*, right; LIN, linear; *M*, magnetization direction; *O*, out of surface; *I*, into surface; *P* vs *M*, relative directions of helicity and magnetization; +, parallel; −, antiparallel; *B*, branching ratio $I(2p^{3/2})/[I(2p^{3/2})+I(2p^{1/2})]$; $B_{\rm exp}$=raw experimental results; $B'_{\rm exp}$, experimental results, normalized to the linear statistical prediction; $B'_{\rm exp}=B^{*}_{\rm exp}(0.67/0.74)$; $B^1_{\rm th}$, atomic theory prediction, $4\mu_B$/Fe atom, 100% polarization; $B^2_{\rm th}$, atomic theory prediction, $2\mu_B$/Fe atom, 100% polarization; $B^3_{\rm th}$, atomic theory prediction, $2\mu_B$/Fe atom, 90% polarization. α is the percent of spin polarization of the unoccupied states (e.g., for $4\mu_B$/Fe, $\alpha=100\%$ or 0%, and for $2\mu_B$, $\alpha=75\%$ or 25%, depending upon the direction of magnetization) and β is the percent of right circular polarization with $\beta=100\%$ for right circular, $\beta=0\%$ for left circular, and $\beta=50\%$ for linear polarization.

P	*M*	*P* vs *M*	$B_{\rm exp}$	$B'_{\rm exp}$	$B^1_{\rm th}$	$B^2_{\rm th}$	$B^3_{\rm th}$
L	*O*	+	0.64	0.58	0.50	0.58	0.60
L	*I*	−	0.83	0.75	0.83	0.75	0.73
R	*I*	+	0.65	0.59	0.50	0.58	0.60
R	*O*	−	0.83	0.75	0.83	0.75	0.73
LIN			0.74	0.67	0.67	0.67	0.67

$B_{\rm th}=[3+2(1-\alpha)\beta+2(1-\beta)\alpha]/6$

from a simple one-electron picture. Much, if not all, of this can be explained using a Slater-integral–based method, including spin-orbit effects [12]. We propose that the nonstatistical effects are the same for linear, right-handed, and left-handed polarized x rays, to zeroth order. Thus, we will "normalize" our branching ratios by multiplying $B_{\rm exp}$ by (0.67/0.74). This normalized B is shown in Table I under the heading $B'_{\rm exp}$. It is important that the previously measured [12] bulk Fe B(linear) is in agreement with our observations for Fe ultrathin films.

Thus, $B'_{\rm exp}$ is a normalized branching ratio, derived solely upon experimental measurements and emphasizing the effect of polarization variation. Its values are only as accurate as the assumption that the nonstatistical effects are the same for right-handed, left-handed, and linearly polarized x rays. The impact of this limitation will become more obvious below. Paralleling the pioneering work of Erskine and Stern [13], we have derived a simplistic model which seems to quantitatively explain our results.

Included in Table I are the predictions of a naive theoretical model, based upon an atomistic, statistical, single-electron picture. What is surprising is not only the high level of quantitative agreement between theory and experiment but also the implied high degree of saturation, i.e., the observation of essentially completeness of the effect. A thorough theoretical analysis of these spectra would require a detailed knowledge of the unoccupied states, including spin and dispersion relations as well as temperature-dependent occupation functions [14]. However, in the absence of that, we have considered a limiting case to provide a naive yet reasonable picture. The assumptions implicit in this model are the following: (1) All transitions are electric dipole, going from the $2p$ to $3d$ states of Fe; and (2) all allowed $2p \rightarrow 3d$ transitions have the same radial probabilities and thus branching ratios of peaks can be derived from the square of the spherical harmonic transition moments, with the appropriate coefficients from a consideration of the $2p^{3/2}$ and $2p^{1/2}$ initial state functions. (It is also necessary to assume either an octahedral splitting of the $l=2$ manifold for each spin, or an equal weighting of all $m_l=2$ states: while perhaps unrealistic it provides a good starting point.) We have also included the effects of varying spin alignment (or moment per Fe atom) and the degree of helical polarization. Using this approach, one obtains $B_{\rm th}$ equation and the "theory" ratios of Table I.

First, consider the raw data ($B_{\rm exp}$) and the extreme limiting case of $3d^6$ Fe with a $4\mu_B$ moment (only minority spin states unoccupied), $B^1_{\rm th}$. Note that even here there is semiquantitative agreement. In fact, the experimental B covers almost 60% of the allowed range predicted for $B^1_{\rm th}$. However, by incorporating normalization to statistical predictions ($B'_{\rm exp}$) and utilizing a magnetic moment of $2\mu_B$/Fe atom as per Refs. [3,7,15], the agreement is nearly exact. For the $2\mu_B$/Fe case, we assume four spins up and two spins down, with correspondingly, three d holes spin down and one spin up. Although this seemingly violates Hund's rules, it is reasonable to expect crystal-field splittings would break the degeneracy [16]. The nearly exact agreement may be slightly fortuitous: both $B^1_{\rm th}$ and $B^2_{\rm th}$ assume 100% circular polarization. Inclusion of a lower degree of polarization [17] ($B^3_{\rm th}$, 90%), lowers the level of agreement slightly, but it still remains within the range of our error estimates (less than 4%).

A word of caution is necessary here. There are many assumptions built into our $B_{\rm th}$ equation, shown in Table I. Perhaps the most important is the normalization of the nonstatistical effects. Thus, even though our $B_{\rm th}$ and $B'_{\rm exp}$ agree so well, it is appropriate to put realistic limits upon the results of the analysis. In essence, the ability to determine magnetic moments in this fashion is probably limited to a single digit differentiation: In this case, we can distinguish $4\mu_B$ from $2\mu_B$. It is probable that, at best, our error bar is $\pm 1\mu_B$. In fact, there is great utility to such a simple analysis, where $B'_{\rm exp}$ is derived solely from experimental data and $B_{\rm th}$ seems to follow such a simple expression. Of course, it is fair to question the generality of this approach and only widespread testing will be definitive. In fact, applying this method to the Ni $2p$ MCD of Ref. [1] and resorting to fractional occupancy, we predict a magnetic moment for Ni of $(0.4 \pm 1.0)\mu_B$/atom, in agreement with previous measurements [18]. While our method can be used to extract a rough estimate of the magnetic moment, greater precision will necessitate more sophisticated methods [19].

Assuming our model is approximately correct, we can then predict the limits over which $B'_{\rm exp}$ (the normalized value) can vary. That corresponds to $\alpha=0,100\%$ and $\beta=0,100\%$: $\frac{1}{2} \leq B_{\rm th} \leq \frac{5}{6}$. Of course, the nonstatistical effects can shift the three values (right, left, and linear) around together, but the helicity effects have finite limits. Within this context, we have observed over 50% of the largest possible range. Thus, we believe that we have observed near-saturation signals, with at most another factor of 2 in B being possible. Moreover, we have observed the entire effect predicted for a $2\mu_B$/Fe atom.

Finally, the effects of coverage and temperature are considered. Using the peak ratios as a measure of magnetization, the following observations were made. (1) Samples required cooling for magnetization. (2) A minimum of two monolayers (ML) was necessary for magnetization; a 1-ML sample would not magnetize, at least not perpendicularly to the surface. (3) It was possible to remagnetize a sample after cooling a previously warmed and demagnetized sample. (4) Variations of the B and thus magnetization could easily be followed as a function of time and temperature. An example of this is shown in Fig. 2, which shows the variation of the B for a 4-ML Fe film in an antiparallel configuration, as it is warmed from 150 to 300 K. (A B near 0.72 corresponds to a loss of magnetization.) These observations are con-

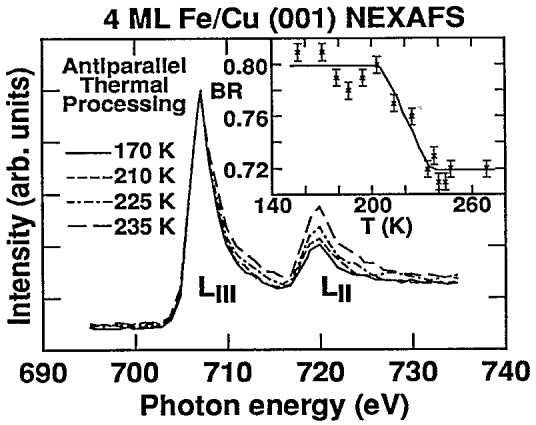

FIG. 2. The temperature dependence of the magnetization, using NEXAFS magnetic circular dichroism as the probe. Absorption vs energy spectra, similar to Fig. 1, are shown, as well as a plot of branching ratio (BR) vs temperature. The spectra are normalized to the maximum of the L_{III} peak. Because of imperfect placement of the thermocouple on the sample plate, the sample temperature may be slightly higher than that shown. Error bars of approximately $\pm 1\%$ are included for comparison but the true error estimate is probably higher.

sistent with and confirm those previously reported concerning this system, using spin-polarized electron spectroscopies [3] and surface magneto-optic Kerr effect measurements [4].

We report here the first observation of perpendicular NEXAFS dichroism in an ultrathin magnetic film. Moreover, a giant effect is observed, bordering upon the limits of complete saturation, including magnetization and helicity polarization. We can explain this giant effect with a simple atomic model, with the data in accordance with a moment of approximately $2\mu_B$/Fe atom. Temperature and coverage studies are consistent with those reported for this system with other techniques. In essence, we have probed the spin polarization in the empty states near E_F of a ferromagnetic system. The large dichroism observed coupled with the high flux available from synchrotron radiation, even for circular polarized x rays, makes this technique of particular importance in studying low-dimensional or dilute magnetic systems.

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